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Microfluidic derivatisation technique for determination of gaseous molecular iodine with GC–MS

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ABSTRACT

Gaseous molecular iodine (I_2) is an important source of reactive iodine in the marine atmosphere, but the sources of I_2 are not well understood due to the lack of an easily accessible, sensitive and robust technique for analysis. In this study a microfluidic derivatisation technique combined with GC–MS has been developed to measure gaseous I_2. Good linearity in the range of 0.2–416 ppb and low detection limits varying from 6 to 25 ppt for different derivatisation reagents have been achieved, which is a substantial improvement in sensitivity compared with the spectrophotometric method (detection limit of 1.20 ppb) in our previous study [L.J. Carpenter, S.M. MacDonald, M.D. Shaw, R. Kumar, R.W. Saunders, R. Parthipan, J. Wilson, J.M.C. Plane, Nature Geoscience, 6 (2013) 108–111]. The microfluidic technique was employed to quantify I_2 produced from the heterogeneous reactions of potassium iodide solution and ozone. Good agreement was observed between the results of the microfluidic technique and the simulation of a coupled surface water–air kinetic model in the amount of I_2 produced on the ozonolysis of iodide solutions.

1. Introduction

Gaseous I_2 is a key source of iodine atoms in the marine boundary layer (MBL) [1]. Atomic iodine reacts rapidly with atmospheric O_3 and the subsequent photochemical cycling results in a reduction in tropospheric O_3 levels [2]. Iodine is also believed to be a source of ultrafine particles in the MBL [3], which can grow to larger particles that contribute to cloud condensation nuclei (CCN) [4] and can potentially influence global climate. Since iodine chemistry was observed to have a significant and extensive influence on photochemical O_3 loss in the tropical Atlantic MBL [5], there has been increasing interest in its sources and atmospheric chemistry. The heterogeneous reaction between aqueous iodide (I^-) and gaseous O_3 was recently postulated to be the main source of oceanic I_2 and hypodiodous acid (HOI) through a series of laboratory experiments [1]. This hypothesis needs to be further verified in the marine atmosphere, but such evaluation is hindered by the lack of sensitive, readily accessible and robust analytical techniques to measure inorganic iodine gases at low concentrations.

Atmospheric I_2 is typically measured by long-path differential optical absorption spectroscopy (LP-DOAS) [6,7]. This technique provides concentrations averaged over a path length of several kilometres and has detected I_2 mixing ratios in iodine-rich coastal regions [7] with a detection limit of 0.5 ppt but is unsuitable for point measurements. Broadband cavity enhanced absorption spectroscopy (BBCEAS) can measure gaseous I_2 in situ and features a significantly higher spatial resolution (less than 1 m) [8]. Combined with good temporal resolution (several minutes) BBCEAS thus complements LP-DOAS in point measurement of tropospheric I_2. Recently, atmospheric pressure chemical ionisation tandem mass spectrometry (APCI-$(MS)^2$) has been successfully applied to measure gaseous I_2 at low ppt levels in oceanic air at the Cape Verde Atmospheric Observatory [9]. The techniques discussed above are technically demanding and unavailable to the majority of laboratories. In recent years the diffusion denuder has been widely employed to measure gaseous I_2 since this technique has the advantage of being straightforward, specific, relatively cheap and portable [10,11]. However, the technique requires several hours of field sampling and involves a series of processes including the denuder preparation, solvent elution, pre-concentration of sample solution and offline analysis by GC–MS [10,12] or a UV/vis spectrophotometer [11]. These labour intensive and complicated processes mean that avoidance of secondary contamination into the samples is a considerable challenge.

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The development of a methodology for gaseous I_2 analysis which can both eliminate the laborious bench processes for sample preparation and utilise the universality of standard analytical techniques could allow more routine analysis of I_2 in the environment and much-needed knowledge on its atmospheric concentrations and distributions. In this work, a rapid, simple and sensitive microfluidic derivatisation approach for I_2 analysis has been developed utilising accelerated and highly efficient derivatisation reactions inside a micro-reactor. This methodology for gaseous I_2 builds on our previous reported microfluidic technique [13,14]. The performance of the microfluidic derivatisation technique for I_2 analysis was evaluated through measurement of I_2 emitted from the interface of aqueous I^- and O_3. The observations were compared with the simulations using a coupled surface liquid–air box model [1].

2. Materials and methods

2.1. Chemicals

All chemicals were purchased from Sigma-Aldrich Company. Solvent methanol (HPLC grade) was bought from Fisher (UK). N, N-dimethylaniline (NDMA), 1,3,5-trimethoxybenzene (TMB), 2,6-dimethylphenol (DMP) were directly utilised as derivatisation reagents. Ultrapure water was provided by the water purification equipment (ELGA-PURELAB flex system, VEOLIA, France).

2.2. Micro-reactor layout and experimental set-up for gaseous I2 measurement

The modular glass microfluidic chip was fabricated by Dolomite Centre, UK. The detailed description of the micro-reactor layout can be seen in our previous work [13,14]. The micro-reactor integrates three key functions: (1) a gas and liquid reactor, (2) sample pre-concentration, and (3) reagent heating. The I_2 sample gases passed into the micro-reactor at 200 mL min^{-1} through inlet 2 and inlet 3 and was helped by a new KNF diaphragm gas pump (PM20994-022, Neuberger, Germany), which is located at the outlet of the sample impinger. The derivatisation solution was introduced into the micro-reactor simultaneously at 60 μL min^{-1} through inlet 1 by a peristaltic pump (Watson Marlow 205S, UK). The sample gas and the solution of derivatisation reagent mix together through the mixing junctions and react in the micro-channel. The reaction solution eluting from the micro-reactor was collected into a sample impinger. The detailed experimental set-up is shown in Fig. 1. About 1.0 mL derivative solution can be obtained after 30 min reaction and further pre-concentrated to 50 μL by a nitrogen flow, prior to GC–MS measurement.

2.3. Generation of standard gaseous I_2

Gaseous I_2 standards were generated using a commercial molecular iodine permeation tube (Kin-TekTM, USA) stored in a permeation oven at 40 °C. Iodine emission rates at the operating temperatures were determined directly by repeated weighing of the tube at four week intervals. The permeation chamber was flushed with zero grade nitrogen (BOC) at a flow rate of 50 mL min^{-1}. The outlet flow was further diluted with a nitrogen flow varying in the range of 0–10.0 L min^{-1} in order to achieve the desired concentration of gaseous I_2. Where required, a needle valve and T-piece was used to ensure that the flow rate of standard I_2 gas remained constant. The experimental set-up is shown in Fig. 1. All flows were exactly controlled to remain constant by mass flow controllers (MKS, UK), which were all calibrated by an air flow calibrator (Gilian Gilibrator-2, Sensidyne, USA). The range of gaseous I_2 concentrations obtainable was 0.2–22 ppb. To minimise the wall losses and photo-degradation of iodine, all tubing and fittings were wrapped in aluminium foil and heated tape to keep the temperature at 60 °C.

2.4. GC–MS conditions

Separation and detection of the iodine derivatives were performed on a GC–MS (Perkin-Elmer, USA) with quadrupole MS and a DB5 column (30 m × 0.25 mm × 1.0 μm, length × internal diameter × film thickness). GC conditions were as follows: the oven temperature was initially set at 80 °C for 1 min, ramped to 230 °C with a temperature ramp of 30 °C min^{-1} and then held at 230 °C for 1 min. The temperatures of the GC inlet and GC–MS transfer line were kept at 250 °C. The GC–MS conditions were same for the NDMA, TMB, and DMP derivatives. The mass spectrometer was operated in scan mode with a mass range of 100–300 Da to identify the most abundant ions of the iodine derivatives. The select ion chromatograms of most abundant ions were used to quantify the derivative concentrations.

2.5. Collection efficiency and reproducibility

To evaluate the collection efficiency (CE) of the microfluidic derivatisation technique for gaseous I_2, a series of I_2 gases in different concentrations were passed through a small downstream vial filled with 1.0 mL of the derivatisation solution in series after passing out from the sample impinger. The collection efficiency was calculated as CE% using $100\% \times (1 - A_v/A_i)$, where A_v and A_i are the amounts of iodine collected in the vial and the impinger, respectively. The

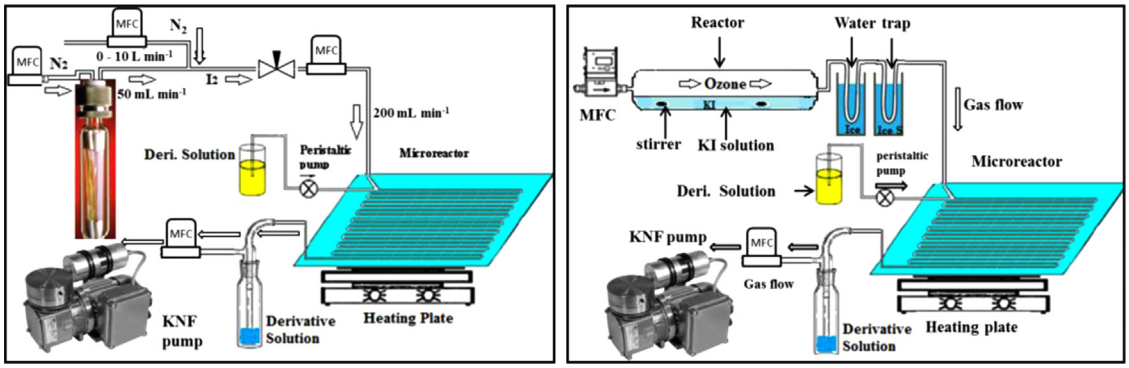


Fig. 1. Schematics of microfluidic derivatisation system for gaseous I_2 produced from permeation tubing (Left panel) and for the determination of I_2 from the KI and O_3 reaction (Right panel).

reproducibility of the microfluidic derivatisation technique was determined by the replicate analyses ($n=5$) of standard I_2 gases at three different concentrations under the same experimental conditions. The reproducibility was expressed as the relative standard deviation (RSD)=[(standard deviation of observed concentration)/(average of observed concentration)] × 100%.

2.6. Measurement of gaseous I_2 emitted from ozonised KI solution

The microfluidic derivatisation technique was employed to measure gaseous I_2 from the heterogeneous reaction of aqueous KI and O_3, which occurred in a cylinder glass reaction vessel (36 cm length × 5.56 cm radius). Iodide solutions (10^{-6}–10^{-5} mol L^{-1} KI), whose concentrations are close to those at seawater surface ([I^-] 10^{-7}–10^{-6} mol L^{-1}) [15] were prepared from phosphate-buffered water at variable pHs and stored in an amber volumetric bottles at 4 °C. The O_3 flow over iodide solution (200 mL) was maintained at 200 mL min^{-1}. O_3 was produced from dry hydrocarbon-free air by its exposure to a UV lamp in an O_3 generator (Part no. 97-0067-02, UVP) and the O_3 mixing ratio [O_3] was controlled in the range 25–250 ppb by adjusting the length of UV lamp exposed to air. The [O_3] were monitored by a model 49i ozone monitor (Thermo Scientific, USA). The above experimental conditions were identical to those in our previous experiment, which is favourable to the comparison between the microfluidic technique and the spectrophotometric method employed in our previous study. During the experiment the entire reaction vessel was covered with aluminium foil to prevent I_2 losses from photolysis. The gas from the outlet of the reaction vessel then passed through two cold traps in series (one at 0 °C and another at −10 °C) to remove the water and was drawn into the micro-reactor to react with the derivatisation reagents (NDMA, TMB, and DMP), respectively. The resulting derivative solution was collected in 10 ml impinger whose outlet was collected by a KNF diaphragm gas pump (PM20994-022, Neuberger, Germany) to keep the gas–liquid flow fluent from microreactor. The gas flow of KNF pump was set at 250 mL min^{-1} by a mass flow controller to avoid an extreme low vacuum in the impinger. The final resulting solution (about 1.0 mL) was pre-concentrated to 50 μL by nitrogen flow and then determined by GC–MS. The schematic of the whole experimental set-up is shown in Fig. 1.

2.7. Modelling iodine emissions

A commercial modelling programme FACSIMILE (MCPA Software) was used to simulate the gaseous I_2 emission from KI solution using a series of chemical reactions involved in interfacial aqueous iodine dynamics, including iodide oxidation, iodine disproportionation, and iodine reduction. Iodine production was initiated by the gas phase flux of O_3 into the interfacial layer containing fixed [I^-]. The interfacial layer was treated as a box, assuming no horizontal advection but mixing vertically with bulk mixed-layer water at a fixed interfacial layer turnover time. A detailed description of the model is given in Carpenter et al. [1].

3. Results and discussions

3.1. Optimisation process

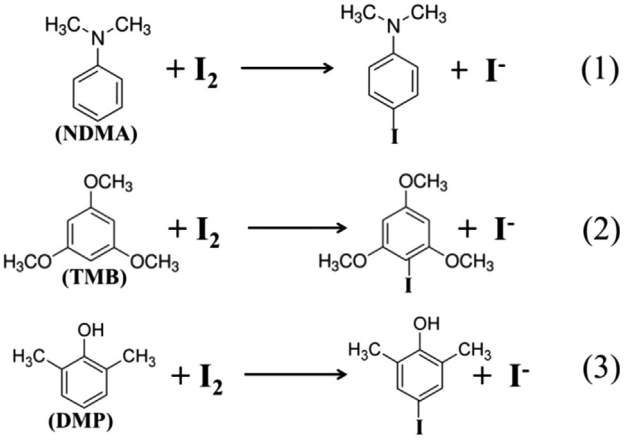
NDMA [10], TMB [12] and DMP [16] have been reported to be effective derivatisation reagents for I_2 in previous publications and thus were chosen in this study. According to our previous experience, the concentration of derivatisation reagents, the solvent, microchip temperature, flow rates of gas and solution, and the reaction time can all affect the reaction efficiency and reproducibility of the derivatisation reaction and an optimisation process of the parameters is required to achieve the highest efficiency of derivatisation from each micro-preparative system. We have undertaken a similar optimisation here to that conducted previously for gaseous carbonyl measurements [13,14]. The optimal conditions for the derivatisations of gaseous I_2 in microfluidic chip are shown in Table 1.

Table 1
Optimal experimental conditions for I_2 microfluidic derivatisation reaction.

Concentration of derivatisation reagent	Temperature (°C)	Flow rate of iodine gas (mL min^{-1})	Flow rate of solution (μL min^{-1})	Solvent
1×10^{-3} mol L^{-1}	60	200	60	Methanol

3.2. GC chromatograms and MS spectra of derivatives

The GC chromatogram (Fig. 2) of each derivative solution contained only one new peak and the mass spectrum of the peak is consistent with that of the derivative formed from the derivatisation reactions of NDMA, TMB, and DMP with molecular iodine; reactions (1), (2) and (3), respectively [16,17].



The selected ion chromatograms of the most abundant ions with $m/z=119$, 121 and 137 Da for the derivatives of NDMA, DMP and TMB, respectively, in the mass spectra (Fig. 2) were used to quantify the derivative concentrations in solutions.

3.3. Method calibrations and detection limits

The method calibration curves for the microfluidic derivatisation technique were established by measuring a series of gaseous I_2 of different concentrations prepared by the nitrogen dilution of I_2 gas emitted from the permeation system under the optimal conditions of micro-reactor (Fig. 1). As Fig. 3a shows, three derivatisation reagents show good linearity on the measurement of gaseous I_2 varying from 0.2 to 22 ppb. The linear equations for I_2 among the three reagents are different in intercepts and gradients.

Above calibration curves are suitable for the measurement gaseous I_2 with its mixing ratio less than 22 ppb. In some cases the microfluidic technique will be employed to measure some gaseous I_2 higher than 22 ppb. Therefore, another calibration method based on the standard solutions of iodine derivatives of NDMA, TMB and DMP at different concentrations was developed to perform the task. In this method the concentrations of iodine derivative solutions have been transferred into the mixing ratios of gaseous iodine assuming the iodine derivatives are formed by

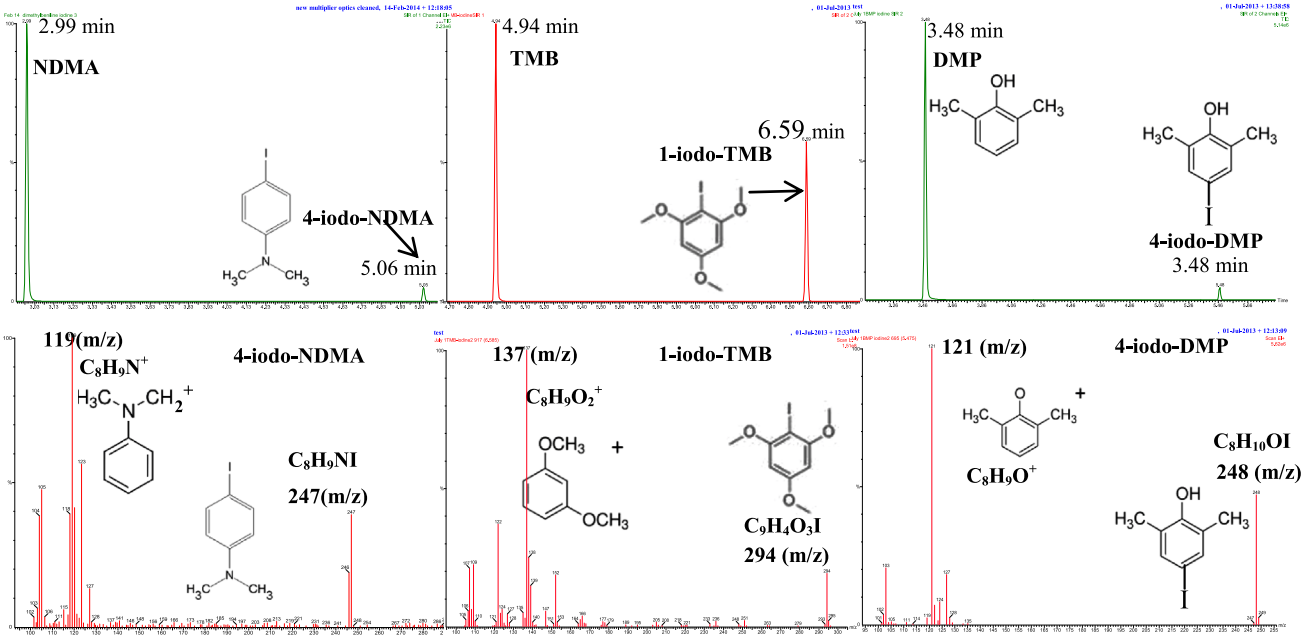


Fig. 2. GC chromatograms of the derivatives and derivatisation reagents (NDMA, TMB, and DMP) (Panels on above row) and mass spectra of the derivatives (panels on low row).

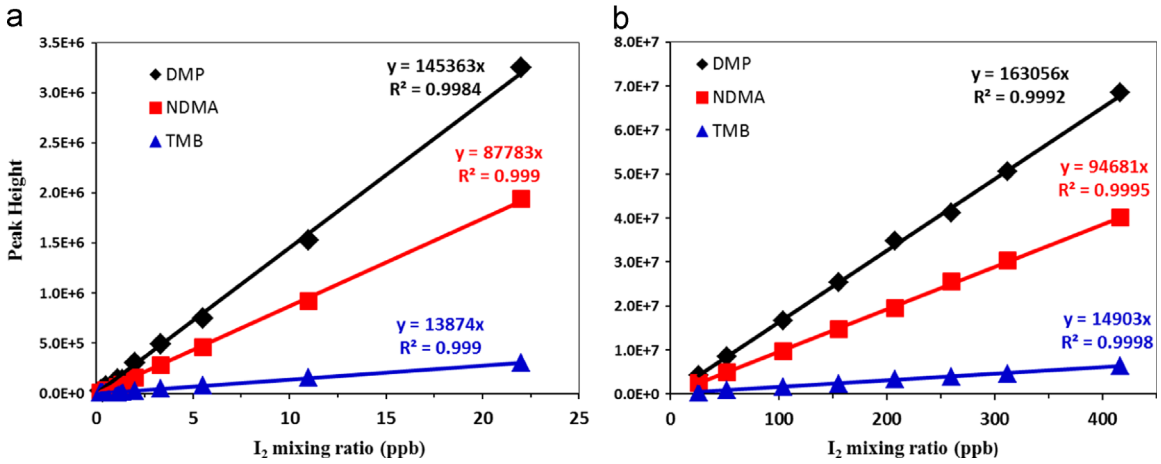


Fig. 3. Calibration curves of iodine derivatives of NDMA, TMB and DMP. (a) Calibrations are based on the derivatisations of standard gaseous I_2 and DMP, NDMA, and TMB, respectively. (b) Calibrations are based on the standard solutions of DMP, NDMA, and TMB derivatives, respectively.

gaseous I_2 and derivatisation reagents at 100% reaction efficiencies. As Fig. 3b shows, the gradients of the calibration curves based on standard solutions are higher than those based on gaseous I_2 derivatisations by 11.5%, 7.9% and 7.4% for DMP, NDMA and TMB, respectively, which may be caused by the lower actual derivatisation efficiencies in micro-reactor than those assumed to be 100% in the standard calibration solutions. The differences in gradient are less than the instrumental errors (15%). Thus, it can be considered that no systemic differences exist in the calibration equations between the standard calibration solutions and gaseous iodine derivatisation, which implies that the calibration solution method is suitable for gaseous I_2 determinations.

Since no signal can be directly observed in the blank samples, we use the standard calculation of the Limit of Detection (LOD) to express the sensitivity of the microfluidic technique. The LOD is determined by the derivative signal which is 8 times higher than the noise ($S/N=8$) in the GC–MS chromatogram. The LODs for gaseous I_2 are calculated to be 6 ppt, 12 ppt and 25 ppt by DMP, TMB and NDMA derivatisations, respectively, for 30 min sampling.

Table 2
Collection efficiency (CE) and reproducibility of the microfluidic derivatisation technique to gaseous I_2.

$[I_2]$ (ppbv)	CE (%)[a]			Reproducibility(%)[b]		
	DMP	NDMA	TMB	DMP	NDMA	TMB
22	94 ± 6	95 ± 4	97 ± 3	6.5	4.3	4.6
11	95 ± 3	96 ± 5	96 ± 2	4.5	5.0	4.2
1.1	98 ± 2	97 ± 3	97 ± 2	3.5	4.4	4.0

[a] CE% using $100\% \times (1 - Av/Ai)$, $(n=5)$.
[b] RSD of replicate analyses $(n=5)$.

These LODs are close to typical concentrations of gaseous I_2 observed above seawater [9].

Collection efficiency (CE) and reproducibility for gaseous I_2 at three mixing ratios are shown in Table 2. All result data indicate that the microfluidic derivatisation technique for gaseous I_2 is satisfactory in CE and reproducibility.

3.4. Application in gaseous I_2 measurement

The microfluidic derivatisation technique was employed to determine gaseous I_2 emitted from the ozonised KI aqueous solution to test the performance of the technique for time resolved measurements. The gaseous I_2 emissions measured by the microfluidic technique through the three derivatisation reagents in Fig. 4 increase near linearly with both [O_3] and [I^-], which is consistent with the observation of previous study[1]. The consistence indicates that the microfluidic derivatisation technique is suitable for the quantification of gaseous I_2. The similar results obtained from DMP, NDMA and TMB derivatisations imply the derivatisation reagents are all feasible and show the same performance for gaseous I_2 derivatisation during the employment of the microfluidic technique. The microfluidic derivatisation measurements of gaseous I_2 emission were compared with the liquid–air model simulations during a series of experiments to investigate the effects of [O_3] and [I^-] on I_2 emission rate. As Fig. 4 shows, the comparisons imply the measurements of the microfluidic technique on gaseous I_2 below 200 ppb are consistent with the model simulations. As the gaseous I_2 concentration increases the discrepancy between the two methods gradually widens. The results obtained from the microfluidic technique were lower by 13.3–30.8% than the model simulations when the mixing ratio of gaseous I_2 are higher than 50 ppb. It has been established that gaseous I_2 is produced from the reaction between O_3 gas and aqueous I^- via the following basic mechanism:

$$H^+ + I^-(aq.) + O_3 \rightarrow HOI(aq) + O_2 \quad (4)$$

$$HOI(aq.) + I^-(aq.) + H^+ \leftrightarrow I_2(aq.) + H_2O \quad (5)$$

$$I_2(aq.) \rightarrow I_2(g) \quad (6)$$

There are four potential reasons for the widen gaps between two methods, which are: (1) the low reaction efficiencies of microfluidic derivatisation to gaseous I_2 at high mixing ratios, (2) dissolution of gaseous I_2 in water contained in the cold traps, (3) the wall loss of gaseous I_2 on tubing and glassware, and (4) processes occurring at high iodine concentrations which are not included in the model. It should be noted that the I_2 losses cannot be quantified using the method in Section 2.5 at high I_2 concentrations since the concentrations of the standard I_2 gas were less than 22 ppb. Hypoiodous acid (HOI) is in equilibrium with I_2 (Eq. (5)) with an HOI/I_2 ratio of less than 0.1 at 10^{-5} M [I^-] solution (pH 8) and about 500 in sea water (10^{-7}–10^{-8} M [I^-]) [1]. The HOI production can result in the less I_2 emission from aqueous solution, which leads to the lower qualifications by the microfluidic technique than those by modelling expectations.

The linear dependence of gaseous I_2 production on [O_3] and [I^-] in this study are consistent with the phenomena observed in previous studies [1,18,19]. Carpenter et al. [1] showed that the emission rate of gaseous I_2 depends primarily on the O_3 flux into the interfacial layer, the surface [I^-], acidity, and mixing of the interfacial layer into bulk water. Due to little competition for O_3 other than reaction with I^-, I_2 production is essentially linear with [O_3]. Both O_3 uptake and O_3 accumulation in the interfacial layer increase with [I^-], thus the net result is a near-linear dependence of I_2 production on [I^-].

The microfluidic derivatisation technique was utilised to investigate the influence of pH on the gaseous I_2 emission from ozonised KI solution. As Fig. 5 shows, the results from the three derivatisation reactions imply that I_2 yields are markedly higher at pH < 4 (pH=2, 3 and 4), remain stable between pH 5 and pH 10, then dropping dramatically to near zero from pH 11 to pH 12. This phenomenon is consistent with the observations in previous reported studies [19,20]. The enhancement of gaseous I_2 production when using acidic KI (aq.) can be explained by reaction (4) and (5), where H^+ is necessary to generate I_2 and high [H^+] is favourable to I_2 formation [19].

4. Conclusions

A new and near automated microfluidic lab-on-a-chip derivatisation technique has been developed for the sensitive measurement of gas-phase molecular iodine (I_2) and has been tested in a series of heterogeneous reactions of KI solution and ozone. The microfluidic derivatisation technique for gaseous I_2 analysis can both eliminate the laborious bench processes for sample

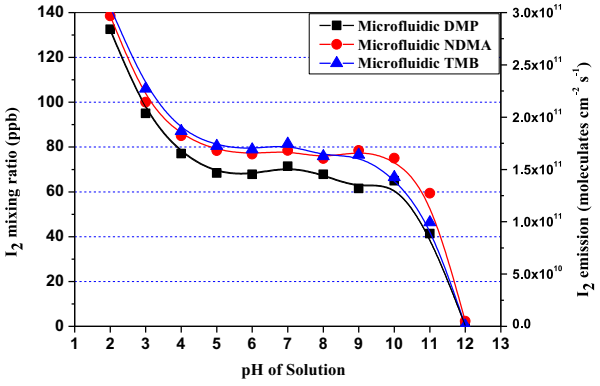


Fig. 5. Microfluidic derivatisation technique employed to study the effect of pH on gaseous I_2 emission. [O_3]: 150 ppb, [I^-]: 3.0×10^{-5} mol L^{-1}.

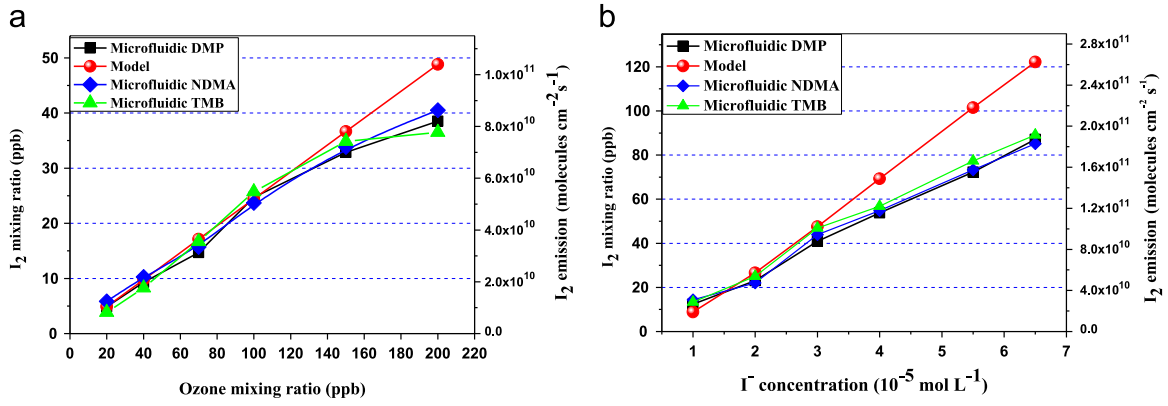


Fig. 4. Comparison between the microfluidic derivatisation technique and model simulation of the effects of [O_3] and [I^-] on gaseous I_2 emission. Experimental conditions for the O_3 effects: 1.5×10^{-5} mol L^{-1} KI, pH=8.0. Effect of I^- concentration: [O_3] 70 ppb, pH=8.0.

preparation and utilise the universality of standard analytical instrument (GC–MS), which could allow more routine analysis of I_2 in the environment. The consistency in I_2 production dependency on $[I^-]$ and $[O_3]$ between the microfluidic derivatisation technique and the simulation of a coupled surface water–air kinetic model provides some initial evidence for the effectiveness of the technique in practical application. The low detection limits varying from 6 to 25 ppt for different derivatisation reagents have been achieved, which is a substantial improvement in sensitivity compared with the spectrophotometric method. Since the detection limits of microfluidic derivatisation technique are close to many reported tropospheric mixing ratios, the microfluidic derivatisation technique could be employed for ambient I_2 measurements with time resolution of 30 min or less.

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